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### **Supporting information**

## Morphology engineering of high performance binary oxide electrodes

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Fig. S1 SEM images of Cu<sub>2</sub>O crystals, including (a) cube, (b)  $\{110\}$  truncated microcubes, (c)  $\{111\}$  truncated microcubes, (d) cuboctahedra.<sup>27</sup>



Fig. S2 SEM images of Cu<sub>2</sub>O crystals. (a) Octahedra, (b) {110} truncated octahedra, (c) 26-facet polyhedra and (d) rhombic dodecahedra.<sup>27</sup> (e) XRD patterns of Cu<sub>2</sub>O crystals.<sup>33</sup>



Fig. S3 SEM images of  $Cu_2O$  polymorphs. The nanoparticle-aggregated spheres (a), nanoparticle-aggregated octahedra (b), {100} truncated octahedra (c) and cuboctahedra (d).<sup>27</sup> XRD pattern of final products.<sup>34</sup>

Table S1 Reaction conditions of 64-kinds Cu <sub>2</sub> O branching structures					
EDTA/Cu	[Cu <sup>2+</sup> ]	pН	Temperature	Time	Results
Molar ratio		1	(°C)	(h)	
1	0.05	8	110	6	Fig. 5, Part I, a1,a2
1	0.05	8	110	12	<b>Fig.</b> 5, Part I, a3,a4
1	0.05	9	110	6	Fig. 5, Part I, b1,b2
1	0.05	9	110	12	Fig. 5, Part I, b3
1	0.05	9	110	24	Fig. 5, Part I, b4
1	0.05	9	120	6	Fig. 5, Part I, c1,c2
1	0.05	9	120	12	Fig. 5, Part I, c3
1	0.05	9	120	24	Fig. 5, Part I, c4
1	0.1	9	110	12	<b>Fig.</b> 5, Part I, d1–d4
1	0.1	9	120	24	Fig. 5, Part I, e1,e2
1	0.1	9	130	24	Fig. 5, Part I, e3,e4
1.5	0.05	8	110	12	Fig. 5, Part III,
					a1,a2, c1
1.5	0.05	8	110	24	Fig. 5, Part III, a3,a4
1.5	0.05	9	110	12	<b>Fig.</b> 5, Part III, b1,b2
1.5	0.05	9	110	24	<b>Fig.</b> 5, Part III, b3,b4
1.5	0.10	10	110	24	Fig. 5, Part III,
					c2–c4
1.5	0.10	11	110	12	Fig. 5, Part III, d1,d2
1.5	0.10	11	110	24	Fig. 5, Part III, d3,d4
1.5	0.10	12	110	12	Fig. 5, Part III, e1,e2
1.5	0.10	12	110	24	Fig. 5, Part III, e3,e4
1.5	0.10	13	120	12	<b>Fig.</b> 5, Part III, f1,f2
1.5	0.10	13	120	24	<b>Fig.</b> 5, Part III, f3,f4
2	0.05	9	100	12	<b>Fig.</b> 5, Part II, a1,a2
2	0.05	10	100	12	Fig. 5, Part II, a3,a4
2	0.05	11	110	12	<b>Fig.</b> 5, Part II, b1–b3
2	0.05	11	110	24	Fig. 5, Part II, b4
2	0.10	12	110	12	Fig. 5, Part II, c1,c2
2	0.10	12	110	24	<b>Fig.</b> 5, Part II, c3,c4
2	0.10	13	120	12	<b>Fig.</b> 5, Part II, d1,d2
2	0.10	13	120	24	Fig. 5, Part II, d3,d4
2	0.10	14	130	12	Fig. 5, Part II, e1,e2
2	0.10	14	130	24	Fig. 5, Part II, e3,e4

# Detail experimental information of EDTA-assisted hydrothermal method

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Fig. S4 XRD pattern of Cu<sub>2</sub>O branching structure, showing the synthesis of phasepure Cu<sub>2</sub>O crystals.



Fig. S5 (a) XRD pattern of  $Cu_2O$  hopper cubes, showing the synthesis of phase-pure  $Cu_2O$  crystals. (b) SEM images of  $Cu_2O$  hopper cubes.

#### CuO/Cu<sub>2</sub>O lithium ion batteries

For lithium ion battery, working electrodes were prepared by mixing CuO/Cu<sub>2</sub>O sample, acetylene black, and poly(vinylidene fluoride) (PVDF) in a weight ratio of 70:20:10. The mixtures were blended with N-methyl-2-pyrrolidone and pasted onto the copper foils. A galvanostatic cycling test of the assembled half cells was conducted on a LAND CT2001A system at a discharge–charge rate of 100 mA g–1 and in the voltage range of 0.01–3.0 V (vs Li<sup>+</sup>/Li). Cyclic voltammetry (CV) measurements were carried out by an electrochemical workstation (CHI 660D) at the scan rate of 0.1 mV/s and with the potential window of 0.01–3 V.

### CuO/Cu<sub>2</sub>O supercapacitors

For the supercapacitor properties, working electrodes were prepared by mixing Cu2O, acetylene black, and polytetrafluoroethylene (PTFE) in a weight ratio of 80 : 10 : 10. Briefly, the resulting paste was pressed onto a sheet of nickel foam at 10 MPa. A classical three-electrode configuration was used in a 2 M KOH electrolyte. A saturated calomel electrode (SCE) was used as the reference electrode, and a Pt wire as a counter electrode. The cyclic voltammetry (CV), and galvanostatic charge–discharge measurements were carried out by an electrochemical workstation (CHI 660D).



Fig. S6 SEM (a), TEM (b, c and f), and HRTEM (d and e) images of the as-obtained CuO nanoribbons with adding 5 mmol NaOH. Inset in (a) is the magnifying SEM image. XRD pattern (g) showing the products are CuO with standard JCPDS No. 72-629.<sup>74</sup>